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Addition of ketene to ethylene oxide

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ADDITION OF KETENE TO ETHYLENE OXIDE

BY

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A

THESIS

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The author is deeply grateful to Dr. Robert R. Russell who suggested this work, and whose guidance throughout the investigation has been invaluable.

J.P.F.

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INTRODUCTION

Since its discovery by Wurtz[1] in 1859, ethylene oxide has been combined with many materials to produce a wide variety of new substances. This is not surprising since the three membered oxirane ring is quite reactive and is thus vulnerable to attack by numerous reagents. One of the more important commercial applications of ethylene oxide is as an intermediate in the preparation of surface active agents. This involves a reaction with long chain carboxylic acids to produce a molecule containing both hydrophobic and hydrophilic characteristics.

Ethylene oxide undergoes attack by substances containing active hydrogen and also by some substances which do not. These two types of reactions and their mechanisms will be discussed below.

The first mention of a compound containing the ketene structure was made by Wedekind[2] in 1902 when he obtained a ketene as a by-product in the reaction between an acid chloride and a terterary amine.

$$(R_1\ R_2)\ CHCOCl + (R)_3N \text{ ---- } (R)_3NHCl + (R_1R_2)\ CCO$$

Numerous studies were made shortly thereafter by Staudinger[3] in which other methods of preparation were devised.

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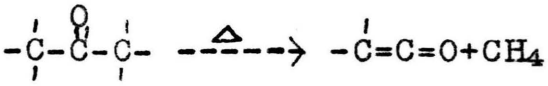
(1) A. Wurtz, Ann., 110, 125-126 (1859).

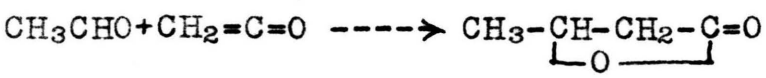
(2) V. E. Wedekind, ibid., 323, 246 (1902).

(3) H. Staudinger, Ber., 38, 1735 (1905).

The method which is used today was developed by Hurd[4] in 1925 and employs the thermal decomposition of acetone.



Since the development and subsequent improvments upon this method have made this process a relatively economical one, ketene has also been allowed to react with a wide variety of reagents. It has found its widest commercial application as an acetylating agent in the manufacture of cellulose acetate and asprin.[5] It may be considered as an anhydride of acetic acid and acts as such forming acetic acid when combined with water. It also forms acetyl chloride when combined with HCl. It is known to react with carbonyl compounds such as acetaldehyde to produce cyclic esters or so called lactones.[6] The reaction may be represented as follows:



Since ethylene oxide may under certain conditions, be considered to be an intermediate in the formation of acetaldehyde, it was thought that it might combine directly with ketene to form the r-butyrolactone. This idea was based upon the fact that in an acid medium before reaction, the eythlene oxide ring should open, thus forming a group which

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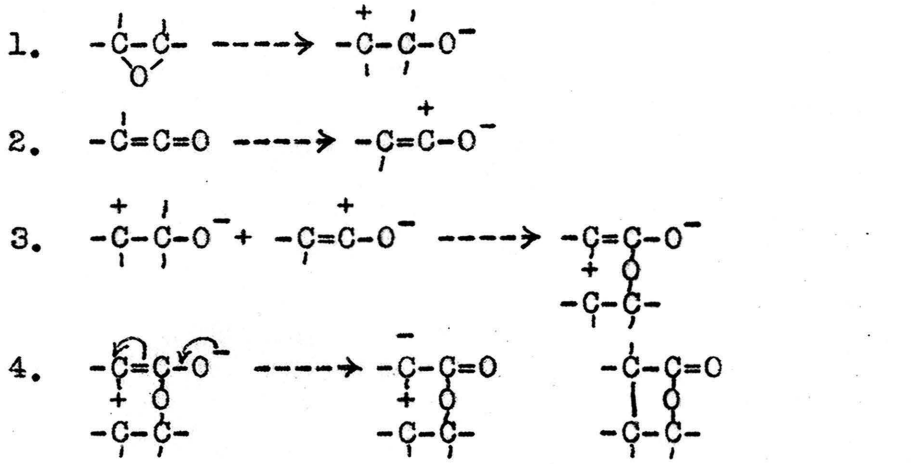
(4) C. D. Hurd, Org. Syn., 4, 39-42 (1925).

(5) "Merk Index," 6th ed., Merk and Co., Inc., Rahway, N. Y., 1952, p. 554.

(6) H. J. Hagemeyer, U. S. Patent 2,469,110 (1949).

would be electrophilic on one end and nucleophilic on the other. This intermediate should then react with the ketene in the following manner:(7)



γ-butyrolactone

γ-butyrolactone has been prepared by a number of methods in the past,(8)(9)(10)(11)(12) however, the commercial preparation(13) is carried out by passing H_2 into 1,4 butane diol vapor in the presence of a copper pumice catalyst at 230°- 250°C.

Some preliminary experiments were carried out to de-

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(7) F. B. Slezak, M. S. thesis, Oklahoma A and M College, 1953.

(8) A. Windaus and G. Klanhardt, Ber., 54, 585 (1921).

(9) S. S. G. Sircar, J. Chem. Soc., 901 (1928).

(10) W. H. Perkin and C. H. G. Sprankling, ibid., 75, 17 (1899).

(11) C. S. Marvel and E. R. Birkhimer, J. Am. Chem. Soc., 51, 261 (1929).

(12) M. E. Carrière, Annales de Chimie, [9] 17, 77-78, 116-117 (1922).

(13) I. G. Farbenind., Deutshes Richspatent, 699,945.

termine whether any new substances were formed in the proposed reaction. The results were positive so the investigation was pursued in a more methodical manner.

The object of this work was to study the reaction between ethylene oxide and ketene, and if possible, to isolate and identify the postulated γ-butyrolactone. Although the results could hardly be described as completly gratifying, they were at least in a sense positive. Many possibilities remain with regard to further modifications of the experimental work on this problem, however it is the author's sincere wish that this investigation will serve some useful purpose in the future.

REVIEW OF THE LITERATURE

A rather extensive review of the literature through 1952 has indicated that no work has been published to the present time on the reaction between ketene and ethylene oxide. It was not until the author made a recent visit to Oklahoma A and M College that he discovered similar work had been done by Frank B. Slezak in 1953 on a graduate fellowship grant from City Service Research and Development Company. The work had not been published, and while the results were essentially negative, the information which it contained was quite valuable.

A review of the production as well as some of the chemical and physical properties of the reactants is given here.

Ethylene oxide is produced by two different processes.[14][15] One is the original process of Wurtz which involves the reaction of ethylene chlorohydrin with lime as follows:

$$ClCH_2CH_2OH + 1/2Ca(OH)_2 \xrightarrow[80mm.]{102^\circ C} -\underset{\diagdown O \diagup}{C}-C- + 1/2CaCl_2 + H_2O$$

The second method involves the direct oxidation of ethylene in the presence of a silver catalyst at 220° to 240°C. The yield is about 50 to 55% based on the ethylene

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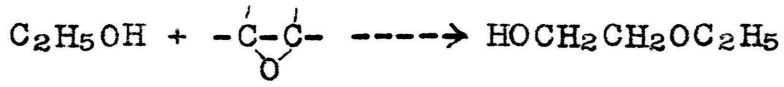
(14) P. H. Groggins, "Unit Processes in Organic Synthesis," 4th ed., McGraw-Hill, New York, N. Y., 1952, pp. 861, 689-690.

(15) G. O. Curme and G. Johnston, "Glycols," Reinhold, New York, N. Y., 1952, chapter 5.

feed. This method is gradually surplanting the previous one.

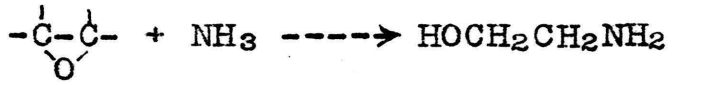
Some of the typical reactions of ethylene oxide may be represented as follows:

1. Alkylation:



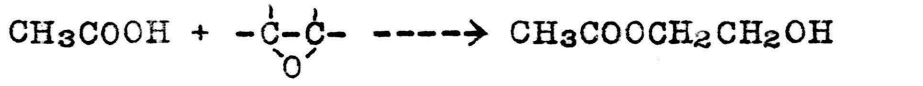
cellosolve

2. Ammonalysis:



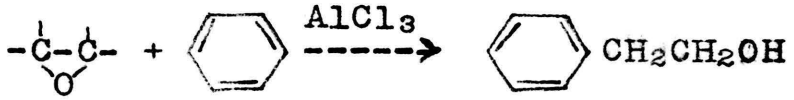
ethanol amine

3. Esterification:



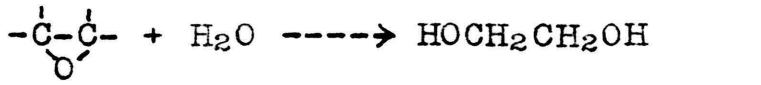
glycol monoacetate

4. Friedel Crafts Synthesis:



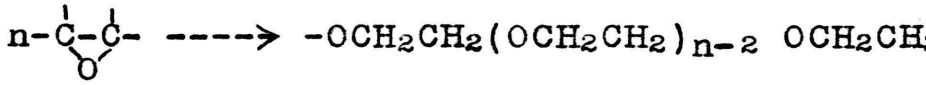
benzyl carbinol

5. Hydrolysis:



ethylene glycol

6. Polymerization:

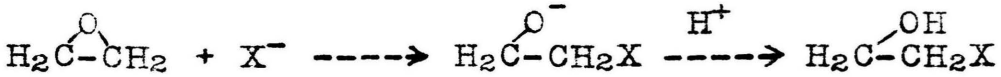


poly ether

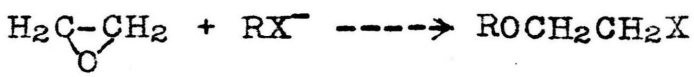
As was mentioned earlier, the reactions of ethylene oxide can be further classified by their behavior with compounds which contain active hydrogen and with those which do not.

The first type, which is the most common, involves a

nucleophilic displacement on carbon which may be represented as follows:(16)



The second type, which is of primary interest in this investigation, involves the opening of the ring in the presence of an acid catalyst, and the subsequent migration of the most positive part of the addendum to the oxygen end of the opened ring and the more negative to the carbon end. This may be illustrated as follows:



For an extensive treatment of the chemistry of ethylene oxide see Elderfield.(17)

A few of the physical properties of ethylene oxide may be listed as follows:(18)

b.p. 13.5°/746.5mm	$D_{10}^{10} = 0.8824$	Soluble: ether
m.p.-111°C	$n_D^7 = 1.35965$	alcohol
Heat of combustion	$C_v = 307.5$ Cal	water
	$C_p = 312.5$ Cal	

Ketene is produced by the thermal decomposition of

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(16) R. C. Elderfield, "Heterocyclic Compounds," Vol. 1, Wiley, New York, N. Y., 1950, p. 27.

(17) R. C. Elderfield, ibid., chapter 1.

(18) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 2, Oxford University Press, New York, N. Y., 1953, p. 504.

acetone as was mentioned earlier.

Some of the typical reactions of ketene may be represented as follows:(19)

1. Hydrolysis:

$$H_2C{=}C{=}O + H_2O \longrightarrow CH_3COOH$$

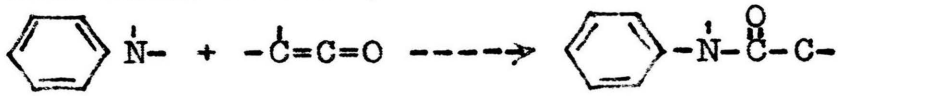
acetic acid

2. Esterification:

$$ROH + H_2C{=}C{=}O \longrightarrow ROOCCH_3$$

an acetate

3. Reaction with amines:



acetanilide

4. Reaction with acids:

$$CH_3COOH + -\dot{C}{=}C{=}O \longrightarrow (CH_3CO)_2O$$

acetic anhydride

A few special reactions of ketene which are of particular interest in this investigation are as follows:(20)(21)

5. Dimerization:

$$2CH_2{=}C{=}O \xrightarrow{50^\circ} CH_2{=}C\underset{\llcorner O \lrcorner}{CH_2}C{=}O$$

diketene

6. Reaction with aldehydes:

$$CH_2{=}C{=}O + CH_3{-}CHO \xrightarrow{ZnCl_2} CH_3{-}\underset{\llcorner O \lrcorner}{CH}{-}CH_2{-}C{=}O$$

β- butyrolactone

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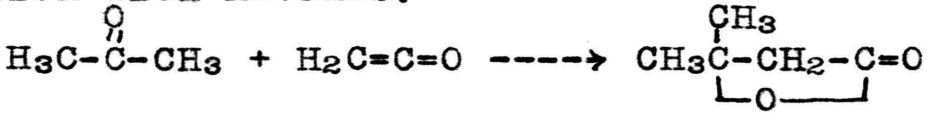
(19) S. C. Wang and F. W. Schueler, J. Chem. Educ., 26, 324 (1949).

(20) H. J. Hagemeyer, J. Ind. Eng. Chem., 41, 765-770 (1949).

(21) J. R. Caldwell, U. S. Patent 2,450,116 (1948).

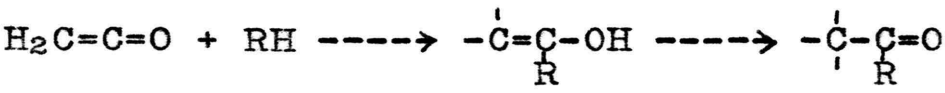
7. Reaction with ketones:



β-methyl β-butyrolactone

It may be seen from the foregoing equations that, like ethylene oxide, ketene reacts with compounds containing active hydrogen directly and also with compounds which do not contain active hydrogen by means of an acid catalyst.

The proposed mechanism for the first type of reaction may be represented as follows:(22)



The mechanism proposed by the author for the second type which includes the reaction in question, has been illustrated previously.

The physical properties of ketene may be listed briefly as follows:(23)

b. -56°	Soluble in acetone
m. -151°	Penetrating odor
MW 42	

(22) F. C. Whitmore, "Organic Chemistry," 2nd ed., D. Van Nostrand Co., New York, N. Y., 1951, p. 345.

(23) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 3, Oxford University Press, New York, N. Y., 1953, p. 143.

EXPERIMENTAL

Ketene was obtained by use of an improved modification of the apparatus illustrated by Wang and Schueler.[19] The ethylene oxide was obtained from a cylinder of the compressed gas.

The reaction was carried out in the liquid phase using dry ether as the solvent. The ethylene oxide was bubbled into an ice cooled gas absorption bottle containing 250 ml. of ether. One gram of boric acid was added and the absorption bottle connected to the ketene generator. The bottle was kept in an ice bath throughout the duration of the reaction. The unmetered ketene was allowed to pass through the ethylene oxide solution for sixteen hours, after which it was assumed that an excess had been added. At the end of this time, the reaction mixture was neutralized with sodium carbonate and extracted with water several times. The ether layer was dried over anhydrous sodium sulfate. After adding an iron nail to prohibit the formation of peroxides, the ether was distilled from the product at atmospheric pressure. The residue was so small as to be almost insignificant. It was a viscous dark brown liquid which was not further identified, but which may have been a polymerization product of one of the reactants. The water layer was acidified and extracted with ether. The ether was dried and distilled in the same manner. The residue again was very small and appeared to be acetic acid. This could be ac-

counted for by hydrolysis of the ketene in traces of water contained in the ether.

The second run was carried out in the same manner the only exception being that the catalyst used consisted of 3 ml. of boron triflouride in ether. It was noted however, that upon addition of the catalyst to the ether solution of ethylene oxide, a definite reaction took place accompanied by the evolution of a gas. This was probably ethylene oxide. A very dark material formed which settled to the bottom of the absorber. The reaction was carried on for the same length of time, and the reaction mixture was neutralized and extracted in the same manner as above. About 10ml. of residue remained after stripping off the ether. It was again dark but less viscous than the former material, and possessed a sweet rather pleasant odor. The water layer apparently yielded the same acidic material as before.

Since 10 ml. was hardly a sufficient quantity to distill in a macro apparatus, it was decided to make a number of runs and combine the residues. This was done, however, on the third run the sintered glass became clogged with the material produced upon addition of the catalyst. A larger reaction vessel was then employed in an effort to produce larger quantities of product, however, the yield did not seem to increase.

When the combined volume of the residue reached about 50 ml., it was fractionated. A vacume system was used, and a pressure of 38 to 40 mm. was employed. The boiling point

increased constantly from 35° to 180°C. The residue, about 20 ml., was black and viscous. The fractions were clear and colorless but possessed a very acrid odor. It was found that each fraction was highly acidic, reacting vigorously with sodium carbonate. This would indicate decomposition of some sort since the original material had been previously neutralized. The acidic fractions, after being neutralized with sodium carbonate, still possessed the sweet odor. This material was salvaged by ether extraction but constituted a very small volume of 10-15 ml.

Several more runs were made and the residues again combined. This time the distillation was done under a vacume of 1.0 to 1.2 mm. in a dry nitrogen atmosphere. Six fractions were collected (a) 25°- 30°C, 5 ml. (b) 30°- 32°C, 15 ml. (c) 32°- 45°C, 4 ml. (d) 45°- 55°C, 10 ml. (e) 55° - 65°C, 7 ml. (f) above 65°C, 20 ml. The residue was a brown rather heavy liquid with very little odor. The other fractions were quite fragrant and possessed no acrid odor whatsoever. Since there was only one fraction which was fairly constant boiling, this material was selected for further study. It was found to be soluble in water and in all the common organic solvents. It did not respond to any of the common classification tests[24] for aldehydes, ketones, acids or alcohols. It did not decolorize Br_2 water or reduce

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(24) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., Wiley, New York, N. Y., 1951, p. 84.

$KMnO_4$. Since the yield was so low and the time required to produce a small quantity was quite appreciable, a saponification was not attempted. This would take a considerable quantity of material, and if the compound were the postulated γ-butyrolactone, it would produce the γ-hydroxy butyric acid. This is a liquid which is soluble in water and which decomposes at room temperature forming the original lactone and water; therefore, it would be of little value. Among the properties listed for γ-butyrolactone are the following:

b_{760}	203-204°C[8]	D^{28}_{28}	1.1054[26]
b_{20}	94[12]	D°	1.1441[25]
b_{12}	89[9]	Misc.	H_2O[9]
$n_D^{26.5}$	1,4343[26]	Reduces Tollens reagent[25]	

Comparison of unknown material with the above data was as follows:

b_{760}	$\approx$190°C	$n_D^{20^{\circ}}$	= 1.4187
D°	1.037	$n_D^{25^{\circ}}$	= 1.4174
Misc.	H_2O		
Tollens test - negative			

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(25) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1953, p. 404.

(26) Beilstein, 2nd Supplement to 4th ed., Vol. 17, p. 286.

Anal. Calcd. for $C_4H_6O_2$: C, 55.80; H, 7.03

Found: C, 53.70; H, 8.43

This would seem to indicate that the compound formed was not γ-butyrolactone, however, it was decided to attempt some further type of reaction which this compound might undergo. After a review of the literature, the method of Huguchi and Zuck[27] was followed in running a titration with lithium aluminum hydride to determine the amount of bound oxygen.

Some of the more common reactions of $LiAlH_4$ with oxygen containing organic compounds are summerized as follows:[28]

1. Aldehydes and ketones:

$$4R_2CO + LiAlH_4 \longrightarrow LiAl(OCHR_2)_4$$

2. Esters and lactones:

$$2RCOOR + LiAlH_4 \longrightarrow LiAl(OR)_2(OCH_2R)_2$$

3. Acid chlorides:

$$2RCOCl + LiAlH_4 \longrightarrow LiAlCl_2(OCH_2R)_2$$

4. Acid anhydrides:

$$(RCO)_2O + LiAlH_4 \longrightarrow LiAlO(OCH_2R)_2$$

5. Alcohols:[27]

$$4ROH + LiAlH_4 \longrightarrow LiAl(OR)_4 + 2H_2$$

6. Acids:[29]

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(27) T. Huguchi and D. A. Zuck, J. Am. Chem. Soc., 73, 2676-2679 (1951).

(28) R. F. Nystrom and W. G. Brown, ibid., 69, 1197-1199 (1947).

(29) R. F. Nystrom 2nd W. G. Brown, ibid., 69, 2548 (1947).

$$4RCOOH + 3LiAlH_4 \longrightarrow LiAl(OCH_2R)_4 + 2LiAlO_2 + 4H_2$$

Almost all the known reactions of lithium aluminum hydride with organic compounds involve a displacement of a strongly electronegative element such as oxygen. Non-polar groups and isolated double bonds do not react. This suggests that the reaction proceeds by a polar mechanism. This might then be a nucleophilic displacement on carbon such as has been discussed previously and may be represented as follows:

$$AlH_4^- + -\overset{\diagdown O \diagup}{\underset{|}{C}}-\underset{|}{C}- \longrightarrow AlH_3 + -\underset{H}{\overset{|}{C}}-\underset{O^-}{\overset{|}{C}}-$$

This proposed mechanism seems to be born out by the work of Trevoy and Brown.(30) It has also been reported in the literature(31)(32)(33)(34) that lactones are reduced to the corresponding glycols by lithium aluminum hydride. A good deal of work has been done in establishing the quantative character of the reaction between $LiAlH_4$ and various reducible groupings. These methods included measurement of evolved hydrogen and potentiometric titration methods. In

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(30) L. W. Trevoy and W. G. Brown, ibid., 71, 1675-1678 (1949).

(31) R. F. Nystrom 2nd W. G. Brown, ibid., 70, 3738-3740 (1948).

(32) R. Mirza, Current Science (India), 21, 195 (1952).

(33) H. E. Zaugg and B. W. Horrom, Anal. Chem., 20, 1027 (1948).

(34) F. A. Hochstein, J. Am. Chem. Soc., 71, 305-306 (1949).

1951, Higuchi and Zuck[27] investigated the possibility of using a chemical indicator. After trying several compounds, N-phenyl-P-amino-azobenzene was found to be superior. This compound, in solution, changes sharply from yellow to red in the presence of excess hydride. The most important phase of the technique involved is in obtaining and maintaining perfectly dry reagents. In a typical determination, a weighed amount of reducible compound is placed in a 125 ml. Erlenmeyer flask and diluted with 15 ml. of dry tetrahydrofuran; 5 ml. of a solution of lithium aluminum hydride in tetrahydrofuran is added and the mixture stirred for one half hour at room temperature under a dry nitrogen cover. After reaction is complete, 5 drops of indicator (.1% solution in dry benzene) are added, and the mixture is back titrated with a standard solution of n-butyl alcohol in dry thiophene free benzene to a permanent yellow end point. Using this technique, Higuchi and Zuck obtained very good results with various oxygen containing compounds. The calculations are as follows:

Gram equivalents in sample = (B-V)M/1000

B = ml. of standard alcohol consumed by the blank

V = ml. of standard alcohol consumed by sample

M = molarity of standard alcohol solution

The data for the titration of the unknown compound is tabulated as follows: n-butyl alcohol = .675M

Wt. slp.	ml. alc. consumed by blank	ml. alc. consumed by sample	differ-ence	No. of gram equi. in slp.	Wt. of 1 gram equi.	Mole. Wt.
.1517	9.5	6.2	3.3	.00222	68.5	34.3
.2938	9.5	3.3	6.2	.00418	70.3	35.2

The molecular weight was determined on the assumption that the unknown compound was a lactone and would exhibit an equivalance of two.

Since not too much experimental work has been done on the reduction of lactones, it seemed in order to attempt such a reduction on a known lactone. It would appear from the work of Zaugg and Horrom(33) that the reduction of some lactones result in rather poor yields. Whether this indicates a lack of quantitative reaction or merely an inability to recover the product is, of course, a question. The lactone chosen was γ-phenyl-γ-butyro lactone.(35) Forty-five grams of this substance in 250 ml. of dry ether were added slowly with constant stirring, to an excess of lithium aluminum hydride in 300 ml. of dry ether. The reaction was carried out under a cover of nitrogen and the reactant added at such a rate as to cause gentle reflux. After all the lactone had been added, the mixture was allowed to stir for twelve hours. The excess $LiAlH_4$ was then destroyed with excess water. The solid material, which was believed to contain the salt of the glycol, was then filtered off and a separation attempted. The results were

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(35) R. R. Russell and C. A. VanderWerf, ibid., 69, 11 (1947).

negative. The wet ether solution was then dried and the ether distilled. There remained a viscous liquid of considerable quantity which upon heating to over 250°C at atmospheric pressure failed to distill. A vacume was then applied and nearly all the material distilled at a constant temperature of 144°C at 1 mm. Almost 30 gms. of this very viscous colorless liquid was collected. This was believed to be 1 phenyl 1,4 butane diol and its presence in the ether layer was explained on the basis that the salt was possibly hydrolyzed by the addition of excess water. It was found, after a review of the literature,(36)(37)(38) that 1-phenyl 1,4 butane diol is a solid. There is, however, quite a differance in melting points reported. Marshall and Perkin report 75°C while Gouge reports 65°C. According to Beilstein, the glycol forms a constant boiling solution with water, boiling at 200°C. This is considerably lower than the observed boiling point. Nevertheless, it was thought that an azeotrope might have been formed, however, all attempts to salt out the alcohol were unsuccessful. Mention is made by Marshall and Perkin that at high temperatures a thick colorless oil distills which they propose might have the following structure:

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(36) R. T. Marshall and W. H. Perkin, J. Chem. Soc., 59, 890-891 (1891).

(37) M. Gouge, Annales de Chimie, [12] 6, 673 (1951).

(38) Beilstein, Main Work, 4th ed., Vol. 6, p. 946.

The physical description is in keeping with the observed facts, however, the proposed structure is hardly likely under the existing conditions. All attempts at preparing a derivative of the substance failed, as did attempts to cause crystallization of the liquid.

SUMMARY

There is some evidence for the formation of an addition compound in the acid catalized reaction between ketene and ethylene oxide. The yield, however, is quite small which makes isolation and identification of the product rather difficult. No apparent reaction took place when boric acid was used as a catalyst, however, some yield was evident when BF_3 was used. Vacume distillation prevents the decomposition of the product. It may well be that under the right set of conditions with the right catalyst the reaction might proceed quite smoothly, however, these conditions or catalysts were not found.

While trying to identify the proposed lactone, a lithium aluminum hydride titration was employed, the results of which, led to a study of the reduction of a known lactone. The lactone chosen was γ-phenyl- γ-butyrolactone. The reaction seemed to proceed smoothly, but the product could not be identified. It is believed that the 1 phenyl 1,4 butane diol is actually formed but fails to crystallize.

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